

# PRODUCTION OF ORGANIC ACIDS IN HIGH YIELDS FROM BROWN COALS THROUGH THE LIQUID PHASE OXIDATION WITH $H_2O_2$ AT LOW TEMPERATURE

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## INTRODUCTION

Low rank coals such as brown coal and lignite are most abundant fossil resources, but they have not been utilized in a large amount because of their low calorific values. They will not be utilized widely without some method that merits the utilization of such coals. Production of valuable chemicals, such as fatty acids *via* liquid phase oxidation may be a possible way to utilize the coals, judging from their structure.

Many attempts have been performed for decades to obtain organic acids from coal through the oxidation in alkali or acid medium. Kamiya et al.<sup>1,2</sup>, Kapo et al.<sup>3</sup> and Bimer et al.<sup>4</sup> oxidized coals by oxygen in an aqueous NaOH or  $Na_2CO_3$  solution at 110 to 270 °C under the pressure of 4.0 to 7.5 MPa. Water-soluble organics could be obtained in 50% yield on carbon basis, but  $CO_2$  was produced in 40 to 50% yield. Montgomery et al.<sup>5</sup> performed the oxidation of a bituminous coal at 150 °C using  $H_2O_2$  as an oxidizing agent, but  $CO_2$  was produced in 60 to 90% yield. Deno et al.<sup>6,7</sup> oxidized four kinds of coals including lignite and several aromatic compounds at 60 to 70 °C using a mixture of trifluoroacetic acid and  $H_2O_2$ . They reported that fatty acids and methanol were produced in 5 to 15% yield.

Thus the attempts for obtaining fatty acids from coal through liquid phase oxidation have not been so successful. A large amount of  $CO_2$  were produced when increasing the decomposition rate by employing severe oxidation conditions such as high temperature, high pressure, and strong acids. A much milder oxidation method seemed to be favorable to produce fatty acids in high yield and in high selectivity. Selection of a suitable coal that is easily degraded in oxidizing agents seemed to be important also.

We have recently found that an Australian brown coal oxidized by  $H_2O_2$  for 2 h at 60°C was extracted by 84 wt% in a mixed solvent of methanol and 1-methylnaphthalene at room temperature<sup>8</sup>. We also analyzed these extracts in detail, then clarified that 40% of carbon in the oxidized coal was aliphatic carbon.<sup>9</sup> This result suggests that a large amount of fatty acids can be recovered if the coal is further oxidized in liquid phase by  $H_2O_2$ .

In this paper we show that the liquid phase oxidation of brown coal with  $H_2O_2$  under mild conditions produces water-soluble fatty acids in high yields. We also examine the mechanism by which the organic acids are produced from coal through a detailed study on the product distribution and the coal properties during the  $H_2O_2$  oxidation.

## EXPERIMENTAL

Three kinds of coals, an Australian brown coal (Morwell, MW), a Canadian brown coal (Highvale, HV), and a Japanese sub-bituminous coal (Taiheiyo, TC) were used as raw coals. The analyses of the coals are listed in Table 1. The coals were ground into fine particles of less than 74  $\mu m$ , and dried in vacuo at 110 °C for 24 h before use. Morwell coal as received, which contains more than 60% of moisture, was also used without drying. This was performed to examine the possibility of utilizing the coal without energy-consuming drying process. The oxidation of the coals were performed as follows: 0.5 g of coal particles were mixed with 10 ml of 30% aqueous hydrogen peroxide in a 500 ml flask with a plug. After treating the mixture for several hours in a water bath kept at a constant temperature of 40 °C, 60 °C or 80 °C, all the gas in the flask was purged by 10 litre of nitrogen gas and was collected in a gas bag. The gaseous product was analyzed for  $CO_2$ , CO and hydrocarbon gases by a gas chromatograph. Next, an excess of cold water was added to the mixture to terminate the oxidation reaction, then the mixture was filtrated to separate it into the solid residue and the aqueous solution. The solid residue was evacuated at 60 °C for 24 h, and was served to the CHN analysis, the F.T.i.r. analysis, and the  $^{13}C$ -n.m.r. analysis. The solid yield on carbon basis was calculated from the CHN analysis. The aqueous solution was served to the TOC, the GPC, and the HPLC analyses. The HPLC analysis detected low molecule fatty acids using a sulfonated polystyrene gel column with an electric conductivity

detector. The content of total organic carbon, the molecular weight distribution, and the composition of fatty acids were estimated from these measurements.

## RESULTS AND DISCUSSION

### Oxidation of dried MW coal

First, the dried MW coal was oxidized at 60 and 80 °C for different reaction times to examine the validity of the proposed oxidation method. Figure 1 shows the changes in the solid yield with the progress of the oxidation. The height of each bar corresponds to the solid yield at a certain reaction time. Elemental composition at each reaction time is given in the bar. At 60 °C the solid yield decreased to 55% in 2 h, and decreased gradually to 19% at 24 h. At 80 °C the coal was decomposed rapidly, and the solid yield was only 15% at 4 h. The water-soluble organics were analyzed by the HPLC and the GPC as stated above. Figure 2 shows a typical chromatogram for low molecule fatty acids obtained using the HPLC. Five components, malonic acid, glycolic acid, formic acid, acetic acid, and a C<sub>7</sub>-calboxyl acid, which could not be identified, were separated distinctly and could be quantified. As an another low molecule component methanol was quantified using the GC-MS method. From these analyses the components whose molecular weights ( $M_w$ ) are smaller than 104 were quantified. Figure 3 shows the change in the number basis molecular weight distribution (MWD) with the progress of the oxidation at 60 °C. Components larger than 60 in molecular weight were detected by the GPC. It is clearly shown that each MWD has two distinct peaks, and that the MWD shifts to smaller molecule region with the increase of the oxidation time. The components detected were separated into two fractions: one is the fraction ranging  $M_w=105$  to 400 and the other is the fraction of  $M_w>400$ . The former fraction was quantified by subtracting the amount of the components ranging  $M_w=60$  to 104, which were quantified by the HPLC. The content of the total organic carbon in the water-soluble product was measured separately. Only CO<sub>2</sub> was detected as the gaseous product, and it was quantified by the gas chromatograph. Using these measurements, we could establish the carbon balance during the oxidation.

Figure 4a shows the changes in the product distribution of carbon basis with the progress of oxidation. At 60 °C the yield of water-soluble components increased gradually with the oxidation time, and reached 52% at 24 h. The yield of the smallest molecule fraction ( $M_w<104$ ) was surprisingly 28%. The yield of CO<sub>2</sub> was less than 30% even at 24 h. At 80 °C the yield of water-soluble components reached 54% only in 1 h, but the yield decreased gradually with the increase of the oxidation time and CO<sub>2</sub> was produced in 50% yield at 4 h. Figure 4b shows the product distribution of the smallest molecule fraction ( $M_w<104$ ) on coal basis. At 60 °C the yield of this fraction increased monotonously with the oxidation time and reached surprisingly 52% at 24 h. At 80 °C, on the other hand, the yield increased little with the increase of the oxidation time, and it was less than 30% at 4 h. The above results clearly indicate that the oxidation of the dried MW coal by H<sub>2</sub>O<sub>2</sub> at around 60 °C is a promising method to produce valuable chemicals in high yield and in high selectivity.

### Test of the validity of the proposed method for other coals

It was clarified that the proposed oxidation method is very effective to produce valuable chemicals from the dried MW coal under mild conditions. Then the validity of the method was tested for several low rank coals and the wet MW coal (coal as received). The coals were oxidized for 24 h at 40, 60, and 4 h at 80 °C. Figure 5a shows the product distribution on carbon basis for the coals. All the coals were decomposed rapidly and a large amount of water-soluble organics were produced at 40 °C and 60 °C. For the MW dried coal, the solid yield was 19% and the yield of the water-soluble organics reached 52% at 60 °C as stated above. The product distributions for the wet MW coal were similar to the distributions for the dried MW coal, although the decomposition rate of the wet coal was slightly smaller than that of the dried coal. This result shows that the drying process of the low rank coal, which consumes a large amount of energy, can be eliminated when the coal was oxidized by the proposed method. For HV, the solid yield was smaller than that of the dried MW coal, but larger amount of CO<sub>2</sub>, 40% in yield, was produced at 60 °C. The main components of the water-soluble organics were high molecular weight compounds. On the other hand, the solid yield was large and the water-soluble organics yield was small for TC coal. This is probably because TC coal (subbituminous coal) consist of more condensed aromatic components as compared with MW coal.

Figure 5b shows the yields of the smallest molecule fraction on coal basis. Only five kinds of fatty acids and methanol were involved in the fraction for all the coals. Such high selectivities for the fatty acids were judged to derive from the structure of coal. Deno et al.<sup>7</sup> performed the H<sub>2</sub>O<sub>2</sub>-TFA-H<sub>2</sub>SO<sub>4</sub> oxidation of model compounds such as toluene and dibenzofuran, and they found that one or two kinds of

particular fatty acids which reflect the structure of the model compound were produced from each compound. The structure of brown coal consists of one or two aromatic rings connected by short chain linkages such as ether, methylene and ethylene bridges. Then the five fatty acids would be produced by the decomposition of the short chains. The total yields of the fatty acids were 10 to 20 wt% at 40°C for all the coals, and they increased to 30 to 50% at 60 °C except for TC coal. The largest yields was obtained for the dried MW coal at 60 °C. It reached surprisingly 52 % as stated earlier, and consisted of 13.1% of malonic acid, 7.8% of glycolic acid, 6.5% of acetic acid, and 19.3 % of formic acid.

Figure 6 shows the MWDs ( $M_w > 60$ ) of the water-soluble compounds for the coals oxidized at 60 °C. They all showed bimodal distributions having peaks at around 200 and 1000. The components of the smaller molecular weight region probably consist of aromatics of one or two aromatic rings. This suggests that much larger amount of fatty acids can be recovered under proper oxidation conditions. Thus it was clarified that the proposed oxidation method is effective to produce valuable chemicals in high yield and in high selectivity especially from the brown coal.

#### Mechanism of the $H_2O_2$ oxidation of coal

It is worth while to examine the oxidation mechanism of brown coal for searching optimum oxidation conditions. This was performed by tracing in detail the changes in the solid properties and the product distributions during the oxidation of the dried MW coal. Figure 7 shows the change in the atomic ratios of oxygen to carbon (O/C) and hydrogen to carbon (H/C) with the oxidation time at 60°C and 80°C. The O/C value increased at first, then decreased with the increase of oxidation time. The H/C value increased significantly with the oxidation time at both temperatures. This clearly shows that hydrogen atoms were introduced into the coal by the  $H_2O_2$  oxidation. Figure 8 shows the change in the F.T.i.r. spectra of the dried MW coal during the oxidation. The intensities of the peaks at  $1710\text{ cm}^{-1}$  and  $1170\text{ cm}^{-1}$ , which are, respectively, assigned to carboxyl groups and alcoholic OH groups, increased with the progress of oxidation. The intensity of the peak at  $2890\text{ cm}^{-1}$ , which is assigned to the aliphatic C-H stretching vibration, increased significantly at 24 h. We clarified that the ratio of aliphatic carbon to total carbon of MW coal is 0.43 from the  $^{13}\text{C}$ -n.m.r. spectrum<sup>9</sup>. The sum of the yields of  $\text{CO}_2$  and the smallest molecule fraction ( $M_w < 104$ ) in Fig. 4a exceeded 0.43 at the oxidation time of 12 and 24 h at 60 °C. This clearly indicates that a part of the aromatic rings of the coal are ruptured by the  $H_2O_2$  oxidation even at 60 °C. The oxidation of coal by air is known to reduces the H/C ratio and the aliphatic proportion in the coal.<sup>10</sup> The above discussion clearly shows that the mechanism of the  $H_2O_2$  oxidation is completely different from the mechanism of the air oxidation. The  $H_2O_2$  oxidation in acid aqueous solutions contains the proton donating reaction.<sup>11</sup> The pH in the mixture of the dried MW coal in the  $H_2O_2$  aqueous solution was below 4.0, so the proton donating reaction surely proceeded to change the coal and the larger molecules of the water-soluble components into aliphatic rich structure. This will surely increase the yields of smaller molecules with the progress of oxidation.

Summarizing the above discussion, the high yield and the high selectivity for the fatty acids were judged to be achieved by the structure of MW coal itself and the proton donating reaction which is realized by  $H_2O_2$  in acid aqueous solutions.

#### CONCLUSION

A new and effective method for utilizing the low rank coal as chemical resources was presented, in which the coal was oxidized with 30%  $H_2O_2$  at below 80 °C under ambient pressure. Oxidizing an Australian brown coal for 24 h at 60 °C, five kinds of fatty acids were recovered surprisingly in 52 % in yield. We are expecting that the proposed method will change the conversion technology of brown coal dramatically.

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Table 1 Properties of coals

Coal(Abbrev.)	Proximate analysis(wt%)			Ultimate analysis(wt%,daf)					
	FC	VM	Ash	C	H	N	S	O	
Morwell(MW)	48.2	50.3	1.5	64.8	4.5	0.6	0.3	29.8	
Highvale(HV)	52.6	35.4	12.0	67.0	4.3	1.0	0.2	27.5	
Taiheiyō(TC)	43.2	45.8	11.0	74.5	6.0	1.3	0.4	17.8	

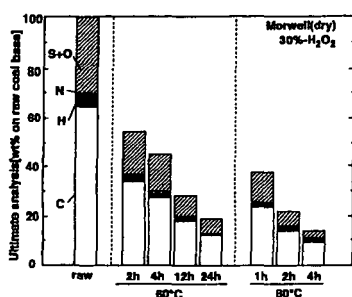
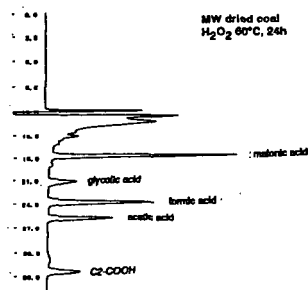
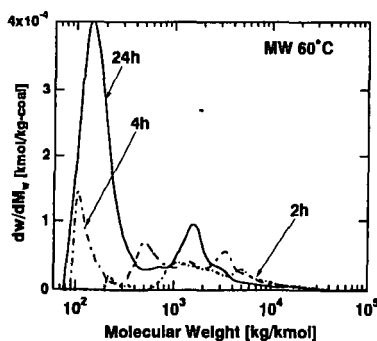
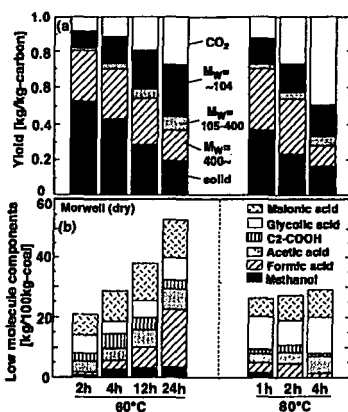
Figure 1 Changes in the solid yield and the elemental composition through the  $\text{H}_2\text{O}_2$  oxidation of the dried MW coal

Figure 2 A typical HPLC chart for the organic acid analysis

Figure 3 Change in the molecular weight distributions of the water-soluble organics produced through the  $\text{H}_2\text{O}_2$  oxidation of the dried MW coalFigure 4 Change in the product distributions through the  $\text{H}_2\text{O}_2$  oxidation of the dried MW coal

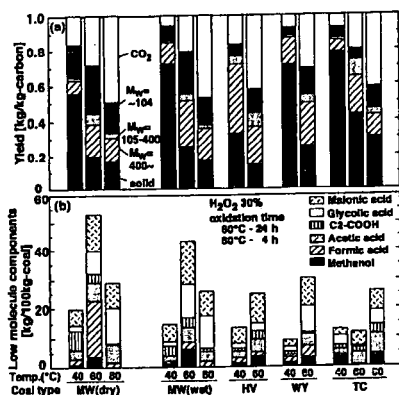


Figure 5 Product distributions through the  $\text{H}_2\text{O}_2$  oxidation for low rank coals

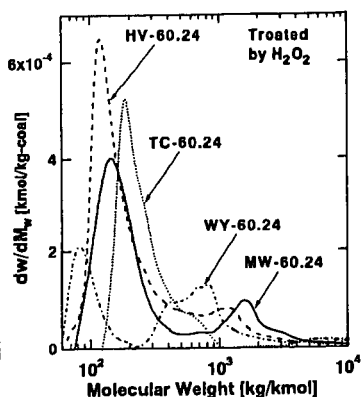


Figure 6 Molecular weight distributions of the water-soluble organics produced through the  $\text{H}_2\text{O}_2$  oxidation for low rank coals

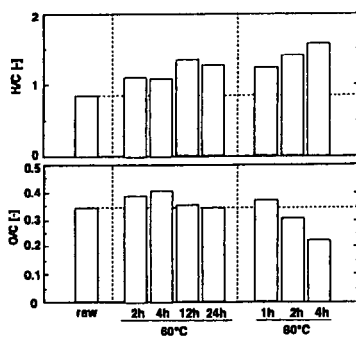


Figure 7 Change in the H/C and O/C atomic ratios through the  $\text{H}_2\text{O}_2$  oxidation of the dried MW coal

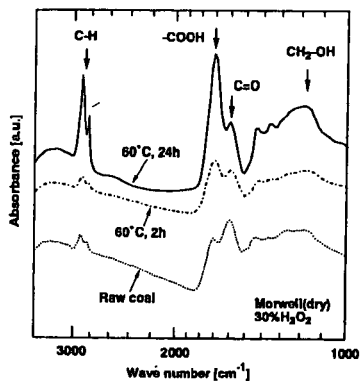


Figure 8 Change in the F.T.i.r. spectra through the  $\text{H}_2\text{O}_2$  oxidation of the dried MW coal